Addendum to the Risk Management Program Guidance for Offsite Consequence Analysis --Performing Analyses for Flammable Substances and Flammable Mixtures

1. Introduction

EPA's Risk Management Program (RMP) requires facilities that have more than threshold quantities of certain hazardous substances in a process to conduct offsite consequence analyses (see part 68 of Title 40 of the Code of Federal Regulations for the full text of this rule). The *Risk Management Program Guidance for Offsite Consequence Analysis*, published by EPA in April 1999, provides specific guidance on how to conduct these analyses. On May 26, 1999, EPA amended the RMP rule (64 FR 28695) regarding certain calculations for worst-case scenarios for regulated flammable substances. This addendum to the April 1999 *Guidance* will help you understand the changes implemented by the amendment and help you make appropriate worst-case calculations. The addendum also provides additional information on performing alternative scenario analysis for flammable mixtures.

For a worst-case scenario analysis under the original RMP rule, the entire quantity from a vessel or process line failure of a flammable liquid or flammable gas was assumed to be released instantaneously and participate in a vapor cloud explosion. Under the amendment to the RMP rule, the quantity of flammable liquid or flammable gas liquefied by refrigeration that can participate in the explosion can be calculated based on volatilization rate. In the original RMP rule, a volatilization rate approach was permitted only for toxic liquids and toxic gases liquefied by refrigeration.

The amendment allows you to calculate the release rate for flammable substances using the same methods that can be used for toxic substances. The release rate calculations for toxic liquids and toxic gases liquefied by refrigeration are found in Chapter 3 of the *Guidance*. Using the toxic liquids methods, you assume that the total quantity in a vessel is spilled onto a flat, non-absorbing surface and forms a pool. You may take passive mitigation systems (e.g., dikes) into account in the worst-case consequence analysis. The total quantity spilled is assumed to spread instantaneously to a depth of one centimeter in an undiked area or to cover a diked area instantaneously. The release rate to air is estimated as the rate of evaporation from the pool (taking into account the required assumption that the temperature of the released liquid must be the highest daily maximum temperature occurring in the last three years or the temperature of the substance in the vessel, whichever is higher). The methods used for toxic gases liquefied by refrigeration are very similar to the methods for toxic liquids.

The equations in Chapter 3 of the *Guidance* can be applied to flammable substances by using the appropriate parameters found in Appendix C of the *Guidance*. Once you calculate the release rate using these methods, you can derive the total amount released to form the vapor cloud explosion. This amount can be used with Reference Table 13 to obtain the worst-case consequence distance as directed in Chapter 5. Specific methods for applying the equations in Chapter 3 to flammable substances are described in the following sections of this addendum.

Note: You are not required to use this new approach to calculate release quantities for worst-case scenarios for flammable liquids and flammable gases liquefied by refrigeration. You may still use the previous method (i.e., assuming that all of the flammable substance volatilizes instantaneously).

2. Flammable Gases, Worst-Case Scenario

The rule was revised so that the total quantity of a flammable gas at ambient temperature is assumed to be released over a period of 10 minutes. However, because the total quantity of the gas is still assumed to be involved in the vapor cloud explosion, there are no changes to the methods for calculating the worst-case scenario for flammable gases.

3. Flammable Gases Liquefied by Refrigeration, Worst-Case Scenario

For flammable gases liquefied by refrigeration, the total quantity in the tank or pipe is assumed to be released instantaneously to form a liquid pool. If there is no passive mitigation present, the liquid is assumed to form a pool one centimeter deep which then volatilizes fully. Therefore, in the absence of mitigation, you should treat the substance as a gas and assume that the entire quantity volatilizes to participate in the vapor cloud explosion.

For releases of flammable gases liquefied by refrigeration into an area with passive mitigation (e.g., a diked area), follow the methods described in Section 3.1.3 to calculate the release rate using the following equations. First, compare the diked area to the maximum size of the pool using Equation 3-6 from the *Guidance*:

$$A = QS \times DF \tag{3-6}$$

where: A = Maximum area of pool (square feet) for depth of one centimeter

QS = Quantity released (pounds)

DF = Density factor (see Exhibit C-2 in Appendix C)

If the diked area is larger than the pool size, the mitigation will not affect the release rate, and you should assume that entire quantity volatilizes. If the pool in the diked area has a depth greater than one centimeter, you can calculate release rate from the diked pool using Equation 3-8 from the *Guidance*:

$$QR = 1.4 \times LFB \times A \tag{3-8}$$

where: QR = Release rate (pounds per minute)

LFB = Liquid factor boiling (see Exhibit C-2 in Appendix C)

A = Diked area (square feet)

After you have calculated the release rate using these methods, you can find the total amount of flammable substance that will contribute to a vapor cloud by multiplying the rate by 10 minutes (as specified in the amendment to the RMP rule). Note that it may be possible for the entire pool

of flammable gas liquefied by refrigeration to evaporate in less than 10 minutes; in this case, you should use the total quantity released from the pipe or vessel as the amount that forms the vapor cloud.

4. Flammable Liquids, Worst-Case Scenario

For flammable liquids, the total quantity in the tank or pipe is assumed to be released instantaneously to form a liquid pool. The amount of substance that volatilizes in the first 10 minutes is assumed to be involved in the vapor cloud explosion. If the spilled liquid is contained by passive mitigation and forms a pool deeper than 1 cm, then mitigation can be taken into account when calculating the amount of substance that volatilizes.

<u>Releases of flammable liquids from pipes</u>: If the liquid is released from a pipe, follow the methods described in Section 3.2.1 to calculate the quantity of liquid released. Calculate the volume of the pipe and then divide by the density factor times 0.033 to obtain the quantity released in pounds. Use the appropriate density factor (DF) reported in Exhibit C-3 of Appendix C.

<u>Unmitigated releases of flammable liquids</u>: For unmitigated releases at ambient temperature (i.e., 25 °C), follow the methods described in the first part of Section 3.2.2 to calculate the release rate, using Equation 3-3 from the *Guidance*:

$$QR = QS \times 1.4 \times LFA \times DF$$
 (3-3)

where: QR = Release rate (pounds per minute)

QS = Quantity released (pounds) LFA = Liquid factor ambient

DF = Density factor

Use the appropriate LFA and DF reported in Exhibit C-3 of Appendix C.

For unmitigated releases at elevated temperature (i.e., above 50°C or at or close to the boiling point), follow the methods described in the second part of Section 3.2.2 to calculate the release rate, using Equation 3-4 from the *Guidance*:

$$QR = QS \times 1.4 \times LFB \times DF$$
 (3-4)

where: QR = Release rate (pounds per minute)

QS = Quantity released (pounds)

LFB = Liquid factor boiling

DF = Density factor

Use the appropriate LFB and DF reported in Exhibit C-3 of Appendix C.

Releases of flammable liquids with passive mitigation: For releases into diked areas or areas with other containment measures, follow the methods described in Section 3.2.3 to calculate the release rate. First, use Equation 3-6 (see above) to calculate the maximum area of the pool. If the maximum area of the pool is smaller than the diked area, calculate the release rate using the methods for unmitigated releases described above. If the diked area is smaller than the maximum pool area, use either Equation 3-7 or 3-8 from the *Guidance*.

For liquids at ambient temperature, use Equation 3-7:

$$QR = 1.4 \times LFA \times A \tag{3-7}$$

For liquids at elevated temperature, use Equation 3-8:

$$QR = 1.4 \times LFB \times A \tag{3-8}$$

where: QR = Release rate (pounds per minute)

LFA = Liquid factor ambient LFB = Liquid factor boiling A = Diked area (square feet)

Use the appropriate LFA or LFB reported in Exhibit C-3 of Appendix C. Make sure that you check for potential overflow from the diked area or other mitigated area (see methods described in Section 3.2.3 of the *Guidance*).

<u>Releases of flammable liquids at temperatures between 25°C and 50°C</u>: For releases at temperatures between 25°C and 50°C (but below the boiling point of the liquid), follow the methods described in Section 3.2.5 to calculate the corrected release rate using Equation 3-11:

$$QR_c = QR \times TCF \tag{3-11}$$

where: $QR_c = Corrected release rate$

QR = Release rate calculated for 25 °C TCF = Temperature correction factor

Temperature correction factors for flammable liquids, which are not provided in Appendix C of the *Guidance*, are included in Exhibit 1 of this Addendum.

5. Estimation of Worst-Case Consequence Distance

After you have calculated the release rate for a flammable gas liquefied by refrigeration or a flammable liquid using one of these methods, you can find the total amount of flammable substance that will contribute to a vapor cloud by multiplying the rate by 10 minutes (as stated in the amendment to the RMP rule). Note that it may be possible for the entire pool of flammable liquid to evaporate in less than 10 minutes; in this case, you should use the total quantity released

from the pipe or vessel as the amount that forms the vapor cloud. You can then use the methods described in Chapter 5 of the *Guidance* to estimate distance to overpressure endpoints.

You can still apply the methods summarized in Section 9.2 for the estimation of release rates for alternative scenarios for flammable substances. This section refers you to Section 7.2 for specific methods and equations that can be applied to flammable substances.

Note that if you make use of the changes summarized here for calculating release rate, Worksheet 3 in the *Guidance* will no longer be applicable for calculating release quantity for flammable liquids and flammable gases liquefied by refrigeration.

6. Flammable Mixtures

Worst-case scenario:

The amendment to the RMP rule does not affect worst-case calculations for mixtures of flammable gases. However, your options for determining offsite consequences for mixtures of flammable liquids and gases liquefied by refrigeration are affected by the amendment. You can now consider release rate (i.e., volatilization rate) of the mixture when estimating the amount of substance involved in the vapor cloud explosion for the worst-case scenario.

To simplify release rate calculations for mixtures of flammable liquids and gases liquefied by refrigeration, you can select parameters to be used in calculations for the whole quantity of the mixture based on the most predominant regulated component of the mixture. Recall that release rates can be calculated using the LFA for flammable liquids at ambient temperatures, the LFA and a TCF for flammable liquid released at elevated temperatures (if appropriate), and the LFB for gases liquefied by refrigeration or for flammable liquids released at temperatures near their boiling point. The DF is also required for calculation where passive mitigation does not apply. Thus, to carry out a simplified release rate calculation for mixtures, find the appropriate parameters (e.g., LFA, LFB, TCF and/or DF) for the most predominant regulated component and apply these parameters to the entire quantity of the mixture. Then, you can follow the procedures described in previous sections of this Addendum to determine release rate and distance to endpoint. Where another parameter is required (e.g., heat of combustion), again apply the parameter value for the most predominant regulated component to the entire mixture.

This method works well for mixtures when the major regulated components have similar heats of combustion. If the major components of a mixture have very different heats of combustion, LFAs, or LFBs, you may want to select parameters for your release rate calculations based on the regulated component with the highest heat of combustion to avoid underestimating the release rate. For example, this would apply if hydrogen, which has a high heat of combustion compared to other regulated flammable gases, were to comprise 40 percent of a two-component mixture of gases liquefied by refrigeration. Alternatively, for a more accurate picture, you can calculate a weighted average of the various parameters used in the calculations.

Alternative scenarios:

This same approach can be used for alternative scenarios involving mixtures of flammable liquids and gases liquefied by refrigeration: you can make alternative scenario calculations for the quantity of the mixture based on the parameters of the most predominant regulated component. Calculations for alternative scenarios for flammable substances are described in Chapter 10 of the *Guidance*. Possible alternative scenarios for flammable substances include vapor cloud fire, pool fire, BLEVE, and vapor cloud explosion.

As in the worst-case calculations, this method should give useful results if the mixture is comprised of components with similar heats of combustion, LFAs, or LFBs. For mixtures containing components with very different heats of combustion, you may want to consider basing your calculations on the regulated component with the highest heat of combustion or deriving a weighted average for the appropriate parameters.

Calculations and assumptions for potential alternative scenarios involving mixtures of flammable liquids and flammable gases liquefied by refrigeration are summarized briefly here.

- <u>Vapor cloud fire</u>: Apply the LFA of the most predominant individual regulated component to the whole mixture to find the release rate. Divide this release rate by the LFL for that same component and use Tables 26 through 29 to find distance to endpoint (make sure you consider dense/buoyant and urban/rural options).
- <u>Pool fire</u>: Apply the PFF of the most predominant individual regulated component to the entire mixture and use this value in Equation 10-1 to estimate distance to endpoint.
- <u>BLEVE</u>: Select the predominant individual regulated component in the mixture and use Table 30 to find the endpoint distance for this substance at the appropriate fireball quantity. If more than one regulated substance comprises a substantial fraction of the mixture, you may want to check the endpoint distances for these other substances in Table 30 to make sure that the distance is not underpredicted.
- <u>Vapor cloud explosion</u>: Use the same methods as provided for the worst-case scenario for flammable mixtures, but assume a yield factor of 3 percent in Equation C-1 or C-2 (rather than the 10 percent factor assumed for the worst-case scenario).

 $Exhibit \ 1$ Temperature Correction Factors for Flammable Liquids Evaporating from Pools at Temperatures Between 25 °C and 50 °C (77 °F and 122 °F)

CAS Number	Chemical Name	Boiling Point (°C)	Temperature Correction Factor (TCF)				
			30 °C (86 °F)	35 °C (95 °F)	40 °C (104 °F)	45 °C (113 °F)	50 °C (122 °F)
590-21-6	1-Chloropropylene	32.80	ND	ND	ND	ND	ND
60-29-7	Ethyl ether	34.43	1.2	LFB	LFB	LFB	LFB
75-08-1	Ethyl mercaptan	35.00	1.2	LFB	LFB	LFB	LFB
78-78-4	Isopentane	27.84	LFB	LFB	LFB	LFB	LFB
78-79-5	Isoprene	34.06	1.2	LFB	LFB	LFB	LFB
75-31-0	Isopropylamine	31.77	1.2	LFB	LFB	LFB	LFB
75-29-6	Isopropyl chloride	35.70	1.2	1.4	LFB	LFB	LFB
563-46-2	2-Methyl-1-butene	31.15	1.2	LFB	LFB	LFB	LFB
107-31-3	Methyl formate	31.75	1.2	LFB	LFB	LFB	LFB
504-60-9	1,3-Pentadiene	42.00	ND	ND	ND	ND	ND
109-66-0	Pentane	36.07	1.2	1.4	LFB	LFB	LFB
109-67-1	1-Pentene	29.96	LFB	LFB	LFB	LFB	LFB
646-04-8	2-Pentene, (E)-	36.34	1.2	1.4	LFB	LFB	LFB
627-20-3	2-Pentene, (Z)-	36.93	1.2	1.4	LFB	LFB	LFB
75-76-3	Tetramethylsilane	26.65	LFB	LFB	LFB	LFB	LFB
10025-78-2	Trichlorosilane	31.85	1.2	LFB	LFB	LFB	LFB
109-92-2	Vinyl ethyl ether	35.55	1.2	1.4	LFB	LFB	LFB
75-35-4	Vinylidene chloride	31.56	1.2	LFB	LFB	LFB	LFB

Notes:

ND: No data available.

LFB: Chemical above boiling point at this temperature; use LFB for analysis.

Based on vapor pressures calculated from the coefficients provided in *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*, developed by the Design Institute for Physical Property Data (DIPPR), AIChE.